

DRAWINGS ATTACHED.

Inventor:—IVIE LEE SMITH.*Date of Application and filing Complete Specification*:
April 21, 1965. No. 16824/65.*Complete Specification Published*: Oct. 25, 1967.

© Crown Copyright 1967.

Index at Acceptance:—C4 S(43Y, 68X, 68Y, 71Y, 72Y, 74Y, 76Y, 708, 716, 729, 730, 753).

Int. Cl.:—C 09 k 1/12.

COMPLETE SPECIFICATION.

Blue Electroluminescent Phosphor.

We, GENERAL ELECTRIC COMPANY, a Corporation organized and existing under the laws of the State of New York, United States of America, having its office at Schenectady 5, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to luminescent materials or phosphors, and more particularly to an electroluminescent zinc sulphide type phosphor emitting blue light under electric field excitation.

Electroluminescent phosphors may be used in electroluminescent lamps or cells wherein a thin layer of phosphor, which may be dispersed in a suitable dielectric medium, is sandwiched between a pair of conducting plates, at least one of which transmits light. The lamp is in the nature of a luminous capacitor, and when an alternating voltage is applied across the plates, the phosphor emits light which escapes through the transparent plate.

It is well-known that zinc sulphide phosphors can be made with electroluminescent emission reaching a peak in the blue region of the spectrum. However, the previous methods of preparation have yielded phosphors either with good brightness and good particle size but poor maintenance of light output, or with good maintenance of light output but low brightness and particles too large for direct use in some electrical devices. Furthermore, the previous methods of preparation of blue iodide-activated electroluminescent phosphors have required complex and expensive processing. Because

of the fluxing action of the co-activator compounds, the previous methods have involved two lengthy firing steps with particle comminution between the two steps. The first step has been to grow crystals of the zinc sulphide matrix itself along with the incorporation of the activator and co-activator at the same time; the second step has been a lower temperature heat treatment designed to remove the damage to luminescence caused by the comminution. During this second step the particles do not substantially grow in size.

Accordingly, the general object of the present invention is to provide an improved method for producing blue emitting electroluminescent zinc sulphide phosphors.

Further objects of the invention are to provide phosphors having relatively good brightness and improved maintenance of light output with particles in size ranges suitable for the usual purposes, and to provide a more economical method for preparing such phosphors.

Using the method of this invention, blue-emitting copper-activated, iodide-coactivated zinc sulphide phosphors of fine particle size can be prepared in a single firing step by employing zinc oxide in the batch to prevent excessive particle growth.

The phosphors of this invention are prepared by mixing zinc sulphide with from 0.15 to 0.74% by weight of copper iodide and from 0.05 to 10% by weight of zinc oxide, and firing in a stagnant air atmosphere at a temperature in the range 850° to 950°C for a period of one to two hours.

Thus, the method of the present invention involves a one-step firing during which the phosphor particles are grown and the activators and coactivators are incorporated into

[Price 4s. 6d.]



the lattice structure. Phosphors prepared in accordance with the prescribed methods have average particle sizes of 5 to 15 microns and provide blue light of equal or greater brightness, with as much as 600% improvement in maintenance, relative to phosphors prepared by prior methods.

The accompanying drawing is a diagram illustrating graphically the chromaticity with basic mixture composition variations in phosphors prepared according to the method of the invention. A preferred mixture consists of zinc sulphide with 0.50% by weight of zinc oxide and 0.50% by weight of cuprous iodide. The mixture is blended, for example by sifting through a silk screen or milling, and then fired for one or more hours at a temperature below the hexagonal-cubic transition point, i.e., in the range of 850°C to 950°C in a stagnant air atmosphere. The duration of the firing time will depend on the batch size of the material being prepared and must be long enough to allow crystal-lite growth to take place throughout the bulk of the material, but will generally require about one hour or more. As is well known in the art, somewhat lower temperatures can be used with longer firing times, and higher temperatures can be used with shorter firing times, to achieve equivalent results. The basic limits on time and temperature combinations in the present instance are that the phosphors cannot be fired at temperatures high enough to cause phase transformations or at temperatures so low that the firing times required are uneconomical. The economy in the latter situation will depend on many diverse factors such as the availability of furnaces and cost of fuel at the location where the work is to be done.

A progressive increase in copper iodide addition to the phosphor crystals at first gives a blue emission colour to the phosphor and then, with more activator being added, causes the colour of the phosphor to progressively change to a green. So too, a progressive increase in zinc oxide content causes the emission colour of the phosphor to become more green. The particular composition limits specified herein have been chosen to achieve desirable combinations of fluxing action (which determines the resulting particle size) with blueness of colour.

The firing may be done by placing the mixture in the inner one of a pair of close fitting silica tubes, the inner tube being inserted open end foremost within the outer. This allows any gases to be expelled and prevents air from diffusing back and causing excessive oxidation of the zinc sulphide. Silica trays or other containers could be used in an equivalent manner, provided any ambient oxygen-containing atmosphere is effectively excluded. In other words, the

firing is done in a neutral atmosphere.

After cooling to room temperature, the fired material is washed in the usual fashion known in the art in dilute acid and in dilute cyanide solution. For instance, it may be washed in acetic acid solution to remove free zinc oxide and then rinsed thoroughly with deionized water. Next it may be washed in potassium cyanide solution and again rinsed thoroughly with de-ionized water. It may be then dried at a low temperature, for instance about 110°C, to complete the preparation.

The use of iodide salts rather than chloride or bromide salts for coactivation of copper activated zinc sulphide type phosphors is known to provide phosphors with better maintenance than obtained with the latter two types of salts. However, as heretofore processed, iodide salts in zinc sulphide firing mixtures cause excessive particle growth so that some means of comminution must generally be used before the phosphor is suitable for lamp application. Effective treatments for reducing particle size after the final heat treatment will usually also reduce brightness or maintenance or both due to effects not now fully understood but which may include surface effects of various types. Thus, prior processing methods have generally involved two heat treatments, one to grow the crystals from powder and to incorporate the copper iodide into the crystals, and the second, after comminution, to heal the damaged particles at a low enough temperature to avoid excessive particle growth. It has been found that the presence of zinc oxide in mixtures of zinc sulphide and cuprous iodide inhibits the fluxing action of the iodide so that products may be obtained after a single heat treatment having suitable particle size ranges without further treatment, such as comminution.

The concentration of zinc oxide in the firing mixtures is quite critical. Increasing amounts of zinc oxide cause decreasing particle growth and at the same time produce a gradual shift in the phosphor colour from blue to greenish blue to blue-green. Therefore, the amount of zinc oxide desired in the phosphor is that amount which will give the desired blueness while reducing the resultant particle size to the desired range. With much more than 10% zinc oxide, the phosphor can no longer be considered to be blue. Since relatively small oxide additions are quite effective in inhibiting excessive growth, phosphors with average particle sizes of 5 to 15 microns and blue emission are possible. This effect is depicted in the graph of the drawing wherein the chromaticity points of three phosphors containing increasing zinc oxide additions are shown. Each of the phosphors contained zinc sulphide and 0.50% by weight cuprous

iodide. The phosphor of point A on the graph also contained 0.50% zinc oxide, point B had 5.0% zinc oxide, and point C 10% zinc oxide. Point D is the locus of neutral white. Point C is in the greenish-blue region, while points B and A are both in the blue region, with B being closer to the green than is A.

A specific example of a suitable phosphor preparation in accordance with the prescribed method is as follows:

Example

Twenty gm of zinc sulphide, 0.10 gm of zinc oxide, and 0.10 gm of cuprous iodide are mixed by sifting through 150 mesh silk sieve cloth. The mixture is then placed in the inner one of two telescoping silica tubes as previously described and fired for two hours at 900°C in air. The phosphor is then washed in successive steps with acetic acid solution, water, potassium cyanide solution, and water; and then dried at 110°C.

Under electroluminescent excitation at 94 volts (rms) per mil and 60 cycles per second in dry chlorinated biphenyl, the phosphor gives a brightness of 1 foot-lambert. The chromaticity is as shown at point A for ZnS: 0.5% CuI, 0.5% ZnO in the graph. The brightness maintenance is 600% of that

of comparable prior art phosphors in terms of time to one-half maximum brightness.

A feature of the invention is the use of zinc oxide to inhibit excessive particle growth during preparation of blue-emitting iodide-coactivated zinc sulphide: copper phosphors so that products with good brightness, maintenance, and chromaticity may be used as obtained, without the need for comminution either during or after preparation.

WHAT WE CLAIM IS:—

1. A method of preparing a blue electroluminescent zinc sulphide phosphor, which comprises mixing zinc sulphide with from 0.15 to 0.74% by weight of copper iodide and from 0.05 to 10% by weight of zinc oxide, and firing in a stagnant air atmosphere at a temperature in the range 850° to 950°C for a period of one to two hours.

2. A blue electroluminescent zinc sulphide phosphor whenever prepared according to the method of Claim 1.

J. W. RIDDING,
Chartered Patent Agent,
33, Grosvenor Place,
London, S.W.1,
Agent for the Applicants.

